§4. Consideration of Measuring Tritium Concentration in Air Using Gas Chromatograph

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An analyzer previously developed for detecting extremely small concentrations of hydrogen in air was evaluated by using it to distinguish hydrogen isotopes. The analyzer utilizes the functions of a gas chromatograph and an atomic absorption spectrophotometer and is based on the reduction reaction of mercuric oxide with hydrogen. Three test samples were used: gas mixtures containing both protium and deuterium with almost equal concentrations of about 5, 20, or 50 $cm^3/1000\ m^3$ diluted in nitrogen. Each measurement was repeated more than 30 times, and chromatograms were obtained for each test sample. Examination of the chromatograms showed that the retention times for the protium and deuterium could be clearly distinguished. The retention times were virtually constant and indistinguishable, independent of the concentration and repetition time. The peak areas for the protium and deuterium were also stable, independent of the repetition time. Moreover, there was a clear linear relationship between the peak areas and concentrations for both elements. These results show that the analyzer can distinguish the two hydrogen isotopes and estimate concentrations of each as small as about 5 $cm^3/1000\ m^3$. They also show that it may be possible to use the analyzer to monitor tritium concentrations in air.

In the present study, gas mixtures containing tritium itself was not used as test samples to avoid contaminating the analyzer with tritium during development. It can be, however, inferred the detection limit for tritium in air based on the results obtained using the mixtures of protium and deuterium without tritium.

The results of measurement of protium and deuterium shows that the analyzer should be able to detect concentration of tritium as small as about 5 $cm^3/1000\ m^3$ in air. Assuming that all tritiated compounds in air have the chemical form HT (H: protium, T: tritium), the concentration of 5 $cm^3/1000\ m^3$ corresponds to 240 Bq/cm^3. Where, it have to be mentioned that a retention time of HT is assumed to be about 18 minutes that can be distinguished from both ones of HH and DD (about 15 and 21 minutes), using a low-temperature separation column (Hydro isopack).

The analyzer should thus be suitable for monitoring the level of tritium at radiation facilities. Japanese law requires regular monitoring of tritium levels in areas where tritium is handled, at the boundaries of controlled areas, and at the exhaust ports of the facilities. The detection limit of the analyzer and the required detection levels are summarized in Table 1. The right column shows the ratio of the detection level of the analyzer to the required level. The ratio shows the allowance of the detection level. For locations where the ratio is larger than unity, the analyzer's ability is sufficient.

Table 1. Detection limit and concentration limits at various locations.

	Concentration	Ratio
• Detection limit	240 Bq/cm^3	1.00
• Work place	10000 Bq/cm^3	41.6
• Boundary of controlled area	1000 Bq/cm^3	4.16
• Exhaust port	70 Bq/cm^3	0.29

The ratios for the work place and the boundary of a controlled area were 41.6 and 4.16 so the analyzer can be used at both locations instead of conventional radiation monitors like ionization chambers and proportional counters, to monitor tritium levels. However, the ratio was only 0.29 for the exhaust port, so it has to be improved its sensitivity to tritium before it can be used to monitor tritium concentration at port locations.

Finally, it need to continue considering furthermore because tritium may exist in the chemical form of HT (H: protium, T: tritium), as an extremely small part of all hydrogen isotopes (supposed major part of HH and small part of HT) in air samples. This is because air itself contains about 500 $cm^3/1000\ m^3$ of hydrogen in the form of HH naturally. For this case, a gas chromatogram obtained by the analyzer must be schematically drawn as shown in Fig. 1. That is, a peak for HT must appear on the tail of a peak for HH. It is very difficult to distinguish the peak of HT from the peak of HH because the peak of HH is huge compared with that of HT. Distinguishing HT from HH is thus a significant problem. As a consequence, a new method for distinguishing HT from HH should be developed.

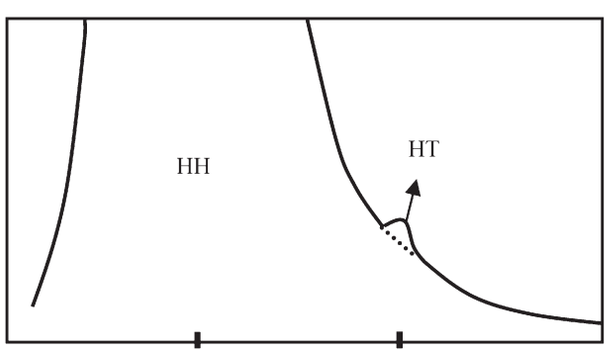

Fig. 1. Imagined hydrogen spectrum of sample gas containing a huge amount of protium and an extremely small amount of tritium.